INFLUENCE OF SURFACE ENERGY ON MELTING

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

WILLIAM ALEXANDER KEMPER

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MELTING TEMPERATURES OF COMPOUNDS ADSORBED ON SILICA GEL

W. A. KEMPER

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

INTRODUCTION

One would expect that the capillary forces believed to be responsible for the adsorption of vapors by silica gel would cause a change in the melting temperature of the adsorbed substance. There is already some evidence for this phenomenon in the behavior of the vapor pressure of adsorbed substances at temperatures below their normal melting points. Coolidge (1) found that the vapor pressure isotherms of benzene on charcoal at temperatures below its normal melting point are curves similar to those at higher temperatures. Furthermore, while the latter curves ran asymptotic to the vapor pressure of normal liquid benzene, the former met at a definite angle with the vapor pressure of solid benzene at the same temperature. This lack of phase continuity between adsorbed and solid benzene was still in evidence at a temperature as low as 40°C. below the normal melting point. Patrick and Land (3) measured the adsorption of iodine on silica gel above and below its normal melting point and interpreted their results as indicating a lowering of the melting point of the adsorbed iodine.

Jones and Gortner (2) have measured the freezing temperatures of water on silica gel with a dilatometer. In these experiments the gel and water were covered with toluene and the volume changes on cooling were noted. The thermal contraction of ice, water, and gel were negligible and that of the toluene present was known. The remaining change was attributed to the expansion of water on freezing. Hence the amount of water frozen at each temperature was calculated. They found that as the temperature was lowered more water continued to freeze, and that even at −48°C. there was still 33 g. of unfrozen water per 100 g. of activated gel. They also found a hysteresis effect in that at a given temperature during cooling there was more unfrozen water than at the same temperature during heating. In repeated experiments the same results were

obtained on heating, only if the cooling had terminated at the same temperature.

Experiments were run with three different concentrations of *gel in water*, but in each case the quantity of water was in excess of that required to saturate the gel. Since this excess froze near 0°C., at lower temperatures there remained saturated gels, all containing the same amount of unfrozen water. Moreover, the results for the amount of unfrozen water at the various temperatures were calculated *per gram of total water present.* However, if the amount of unfrozen water *per gram of dry gel* had been tabulated instead, the results of all three experiments would have been seen to be nearly identical.

The dilatometric method raises two questions. First, what is the effect of immersing the system in toluene? Since the water–toluene interfacial tension is only half that of water–air, larger effects would be expected from capillary forces in the absence of toluene. Secondly, can density changes caused by the negative pressures from these capillary forces be neglected? These negative pressures are greatest on the last-remaining unfrozen water.

Swain and Porter (8) measured the specific heats of argon and hydrogen absorbed on charcoal from 6–50°K. without finding any breaks indicating a sudden change of phase. The specific heats were observed to be less than that of either the solid or the liquid form of these respective elements.

In the present paper a calorimetric method was used to detect any heats of transition attending melting. Specific heats were measured by the Andrews calibrated heat conduction method (5), which is both rapid and continuous. Since it is continuous no intervals are omitted in which a change of phase could escape detection.

APPARATUS AND PROCEDURES

The apparatus is shown in figure 1. The heat is supplied to the calorimeter across an oxygen-filled space separating the calorimeter from an electrically heated, concentric, heavy copper cylinder. The same temperature head is always maintained from the cylinder to the calorimeter, hence the rate of heat transfer to the calorimeter at a given temperature is always the same. Measurements are made of the time required for the temperature of the calorimeter to be raised through successive increments. Two runs with different amounts of a substance of known specific heat give the rate of heat input and the specific heat of the empty calorimeter as functions of the temperature. These functions are used to translate heating times into specific heats of the contents of the calorimeter.

The temperature head and temperature of the calorimeter can were measured by calibrated copper–constantan thermocouples (6) in conjunction with either a White double potentiometer or two type K potentiometers. D'Arsonval galvanometers were used, giving a scale sensitivity of 1.3 to 2.0 mm. per microvolt.

The heat was distributed in the calorimeter can by thirty-four radial fins of 2-mm. brush copper. During a run the temperature at the center of the calorimeter was only 1.5°C. less than at the wall.

An improvement in the apparatus was made by grounding the outer cylinder. This led stray voltages off the thermocouples and the anomalous results previously found (5) at 0°C., where the thermocouple voltage changes sign, were not experienced. Another modification was the chromium plating of the outside of the calorimeter and of the inside of its containing cylinder.

Identical preparations were made for each run. The calorimeter can and the space between the can and the outer cylinder were rinsed three times with boiling acetone, then dried by heating in a current of dry oxy-

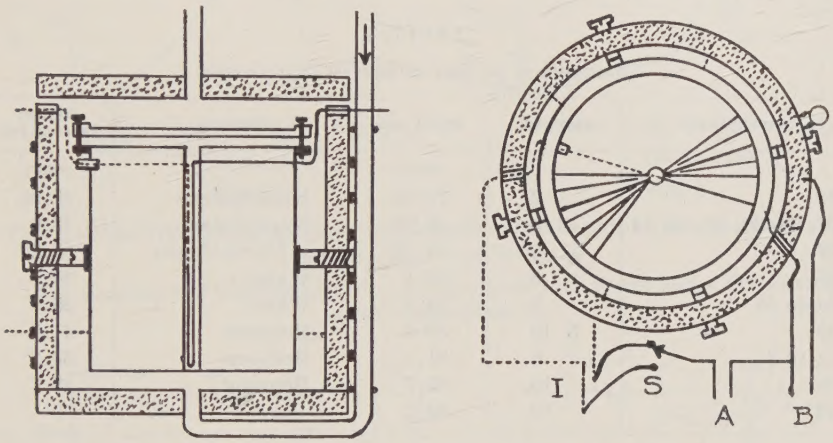

FIG. 1. Vertical cross section of the calorimeter and view from above. I, ice junctions; A, leads to potentiometer indicating temperature at center with knife switch S in upper position and of the wall when in lower position; B, leads to potentiometer for average temperature head. ($\frac{1}{4}$ actual size.)

gen. The calorimeter was then filled and sealed, and the space between the cylinders was swept with oxygen for another half-hour before cooling to the starting temperature. It is essential that the rubber tubing on the inlet oxygen line does not give off condensable vapors. It was found economical to cool first with half a pound of solid carbon dioxide before adding liquid oxygen. When cooling was completed, the inlet oxygen valve was closed and a large heating current was applied until the 1000 microvolt head was obtained. Then, while this temperature head was carefully maintained by manipulation of the vernier adjustment of a series resistance, the times required for each increase of 100 microvolts in the temperature of the calorimeter can were measured with stop watches.

Naphthalene was used as the empirical standard for the calibration.

Wherever available Southard's values (7) for its specific heat were used. Two sets of runs with 22.4 and 71.62 g. of naphthalene gave the rate of heat transfer to the calorimeter and the heat capacity of the empty calorimeter as functions of the temperature.

Silica gel from the Silica Gel Corporation of America was purified by digestion in nitric acid on a steam bath for several days. It was then thoroughly rinsed many times with distilled water during several weeks and finally dried in an oven at 110°C.

The gel was activated by heating for about eight hours at 360°C. in a stream of dried air. The weight of water per unit weight of anhydrous gel was then 3.25 per cent. In this paper the term "activated gel" will represent gel of this water content.

TABLE 1

Amounts of gel and sorbate in experiments

EXPERIMENTS	FIGURES	SILICA GEL	SORBATE	WEIGHT OF SORBATE
		grams		*grams*
52	2	73.63	Naphthalene	35.96
37, 38, 39, 40, 42, 43	8	48.75	Naphthalene	22.9
57	4	69.22	*p*-Nitrotoluene	39.26
35	3	52.1	Water	30.1
44 to 48	7	53.3	Water	26.9
19	5, 10	86.6	Benzene	41.8
21 to 24	6	81.3	Benzene	33.2
16	10	82.7	Benzene	25.7
14	10	83.2		0

The sorption was carried out by mixing gel and sorbate in a heated glass-stoppered bottle on a shaking machine for about twelve hours. The shaking was continued until the gel cooled to room temperature. With naphthalene 70°C. was sufficient for rapid adsorption. A higher temperature resulted in a grey discoloration.

OBSERVATIONS

In figures 2, 3, 4, and 5 (see table 1), the observed times of heating are plotted for typical experiments with silica gel and naphthalene, water, *p*-nitrotoluene, and benzene, respectively. In these experiments a little more of the sorbate was present than was necessary to saturate the gel. The melting of this excess can be seen at the indicated normal melting points. There was also a large heat capacity for the system over a wide temperature interval at a lower temperature. This is taken as evidence of the melting of the adsorbed phase. The actual values for the heat

capacity of the adsorbed substance, which are calculated later in this paper, are consistent with this interpretation.

The curves in figures 6, 7, and 8 (see table 1) demonstrate a hysteresis phenomenon. The results were dependent, in the manner shown, upon the lowest temperature to which the system had been cooled previously.

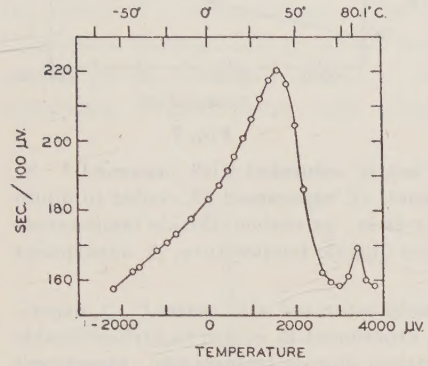

FIG. 2

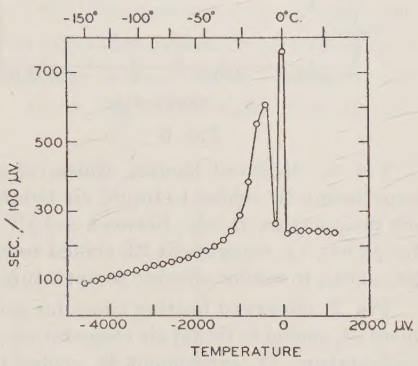

FIG. 3

FIG. 2. Observed heating times for gel saturated with naphthalene and a little excess naphthalene, experiment 52

FIG. 3. Observed heating times for gel saturated with water and a little excess water, experiment 35

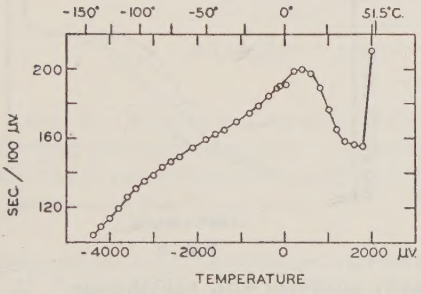

FIG. 4

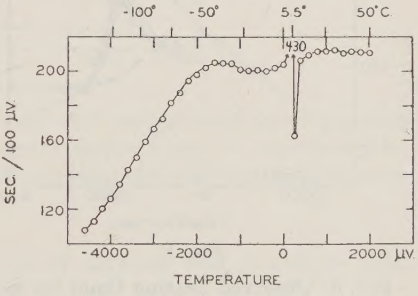

FIG. 5

FIG. 4. Observed heating times for gel saturated with *p*-nitrotoluene and a little excess *p*-nitrotoluene, experiment 57

FIG. 5. Observed heating times for gel saturated with benzene and a little excess benzene, experiment 19

However they were quite reproducible when starting from the same low temperature, and, as far as could be determined, were independent of the rate of cooling or heating.

Figure 9 illustrates how hysteresis in the melting of the adsorbed material could bring about these effects. The slopes of the curves of figure 9,

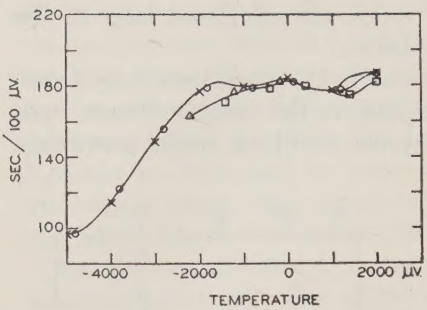

FIG. 6

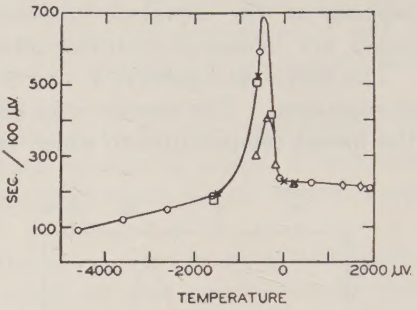

FIG. 7

FIG. 6. Observed heating times for gel nearly saturated with benzene.[1,2] ×, experiment 21, cooled to liquid air temperature; ○, experiment 22, cooled to liquid air temperature slowly, between ±3.5°C. for 48 hr., at carbon dioxide temperature for 18 hr.; □, experiment 23, cooled to carbon dioxide temperature; △, experiment 24, cooled to carbon dioxide temperature.

FIG. 7. Observed heating times for gel nearly saturated with water.[2] ○, experiment 44, cooled to liquid air temperature; ×, experiment 45, cooled to carbon dioxide temperature; □, experiment 48, cooled to carbon dioxide temperature, experiment interrupted at −780 microvolts and held between −780 and −730 microvolts for 3.5 hr.; △, experiment 46, cooled to −20°C.; ◇, experiment 47, started from room temperature.

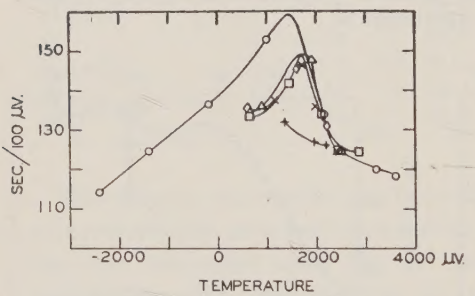

FIG. 8

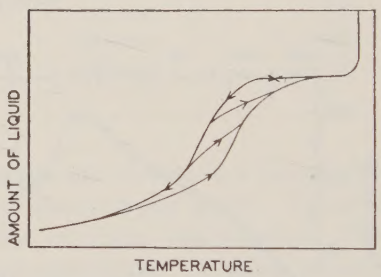

FIG. 9

FIG. 8. Observed heating times for gel nearly saturated with naphthalene.[2] ○, experiment 37, cooled to −89°C.; △, experiment 42, cooled to 2.5°C. rapidly; □, experiment 39, cooled to 5°C. slowly; ◇, experiment 40, cooled to 5°C.; ×, experiment 43, cooled to 5°C., then heated to 15°C. at 2.5 times the usual rate, before taking readings; +, experiment 38, started at room temperature.

FIG. 9. Hypothetical curve, showing hysteresis in amount of liquid in gel

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[1] In order to simplify the curves only every fifth point and the last point were plotted.

[2] The differences in experiments 21, 22, and 23 at the high-temperature end of the curves were due to different rates of evaporation of benzene from the calorimeter, which was not sealed vapor-tight. Because of previous loss, the vapor pressure of benzene was less in the following run.

which represent the amount melting per degree rise in temperature, are similar to the curves in figures 7 and 8. This is the same as the hysteresis in adsorption and desorption measurements with the amount of melt corresponding to the amount adsorbed.

Figure 10 shows typical curves obtained with different concentrations of sorbate. The high values at the low-temperature end of the curves are the result of a complication. The lid of the calorimeter did not seal on tight, and, during cooling, oxygen from between the cylinders was adsorbed on the gel in some experiments. During the measurements the heat of desorption caused these high values. It is apparent that this effect

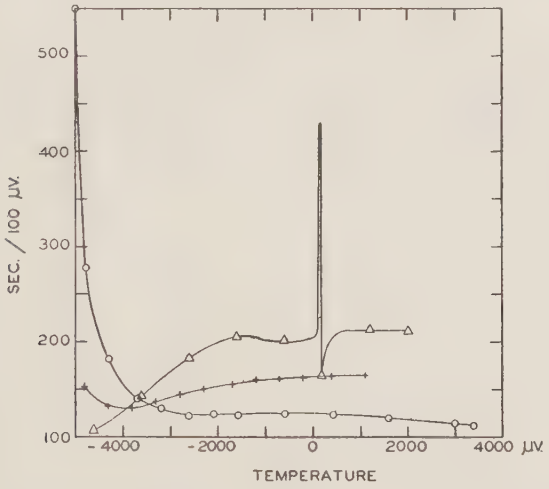

FIG. 10. Observed heating times for silica gel with various amounts of benzene, showing desorption of oxygen.[2] ○, experiment 14, activated gel; +, experiment 16, gel with 31 per cent benzene; △, experiment 19, gel saturated with benzene and some excess.

diminishes with increasing concentration of sorbate and is absent with saturated gels.

TREATMENT OF OBSERVATIONS

The heat capacities were calculated from the times of heating. The heat capacity of the sorbate was obtained by subtracting from the heat capacity of the gel and sorbate that of the gel present.

The heat capacity of activated silica gel, as measured in experiment 14, is given in the third column of table 2. However, because of the desorption of oxygen, only those values above 0°C. were used in the calculations of the heat capacity of the sorbate. Below 0°C. estimated values, shown in the last column, were used instead. These were the sum of the heat

capacity of silica as measured in this apparatus and that of 3.25 per cent ice as given in the International Critical Tables. The heat capacity of silica was the average of two runs (Nos. 9 and 10, table 2) with 167 g. and 205 g. of Merck's C.P. sea sand. The average difference between 9 and 10 was 0.85 per cent, and their mean averages were 3.3 per cent higher than the values of Simon (4).

Values for the difference in the heat capacity of the sorbate in its adsorbed and normal state are recorded in table 3 and some are shown in figure 11.[3] The values are for the amount of sorbate associated with 100 g. of activated gel, rather than per gram of sorbate, in order that the contributions of the various portions of the sorbate under different capillary forces may be additive instead of averaged, and that the results may be independent of the amount of excess sorbate which has normal heat capacity.

TABLE 2

Specific heats used in calculations

Values are given in calories per degree per 100 grams

TEMPERATURE	HEAT CAPACITY OF SILICA	HEAT CAPACITY OF ACTIVATED SILICA GEL	
	Average of runs 9 and 10	As measured in experiment 14	Estimated
°k.			
126	5.45	48.6	8.8
147	6.08	30.2	10.7
167	6.82	23.0	12.0
184	7.47	20.1	13.1
201	8.01	18.4	14.1
217	8.44	17.8	14.8
232	8.92	17.5	15.7
246	9.38	17.3	16.6
260	9.83	18.2	17.4
273	10.27	18.9	18.3
286	10.65	19.2	
299	11.00	19.8	
311	11.28	20.1	
323	11.56	20.5	
334	11.80	20.8	
346	12.03	21.3	

Table 3 shows that at temperatures below its normal melting point the heat capacity of the sorbate is in excess of its normal heat capacity. If the sorbate is condensed in capillaries in the gel, then the difference is accounted for as follows: (*1*) by the heat of fusion of sorbate melting at

[3] See also figures 3 to 6 of the second paper on this subject (J. Phys. Chem. **42**, 381 (1938)).

lower temperatures; (*2*) by the heat of wetting of the gel by the melt; (*3*) by the heat of compression due to diminishing surface forces; and (*4*) by the difference between the specific heat of the melt and that of the normal solid. The difference increases with rising temperature to a maximum below the normal melting point. At this temperature presumably most of the sorbate is now melted. At the normal melting point the heat of fusion of only the excess sorbate is observed.

These values are given in the last row (opposite "n.m.p."). Above the normal melting point, the differences are small. They are partly due to vaporization of the sorbate from the calorimeter, which absorbs heat. Such loss also makes the estimate of the amount of sorbate in ensuing runs

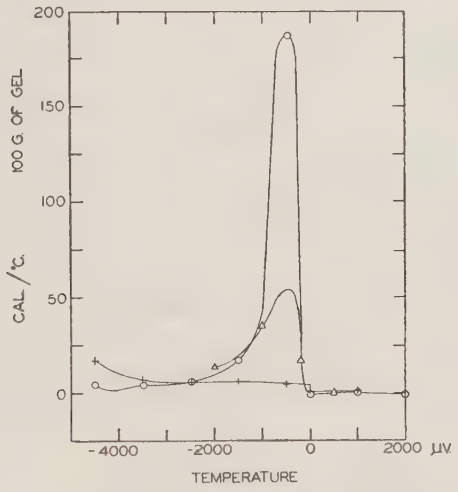

FIG. 11. Heat capacity of adsorbed water in excess of normal heat capacity of water. +, experiment 36, gel 7.1 per cent saturated; △, experiment 51, gel 37.4 per cent saturated; ○, experiment 44, gel 91.4 per cent saturated.

too high. For this reason the results for benzene are not in as good agreement as those for the less volatile sorbates. It is to be noted that these differences are especially small in comparison with the total measured heat capacity of the systems, which, for example, for experiment 44 at 286°K., is 70.2 cal. per degree.

Figure 11 indicates how the results depend upon the composition of the gel–sorbate system. In experiment 36 the gel was 7 per cent saturated with water. Since the surface forces on this small amount of sorbate would be large, it would be expected to be liquid over most of the interval shown. The result then would be the difference in heat capacity of supercooled water and ice. At low temperatures the values are high because of the desorption of oxygen. The results for the 37 per cent saturated

TABLE 3

Heat capacity of substances on silica gel less their normal heat capacity

	BENZENE			WATER							NAPHTHALENE		*p*-NITRO-TOLUENE*
Experiment	17	21	19	36	51	44	45	48	35	49	50	52	57
Moles per 100 g. of gel	0.542	0.544	0.618	0.217	1.145	2.8	2.8	2.8	3.21	5.36	0.367	0.378	0.413
°K.	CALORIES PER DEGREE PER AMOUNT OF SORBATE ASSOCIATED WITH 100 G. OF ACTIVATED GEL												
126	4.3			17.1		3.7							
147	2.6	2.9	2.8	9.2		2.1			2.8				2.8
167	3.7	2.6	1.6	7.1		3.7			3.3				1.3
184	4.5	3.3	2.8	5.8		5.1			5.1				2.0
201	5.5	4.4	4.0	5.4		6.5			6.5				1.6
217	5.6	4.5	5.0	5.0	13.0	9.2			9.7	7.7	4.8	4.0	1.4
232	4.7	3.5	5.4	5.7	19.3	16.5	15.7	16.0	18.6	16.8	3.6	3.4	1.4
246	2.7	1.2	4.6	4.6	35.5	42.9	41.1	41.5	34.8	41.1	3.5	3.4	1.5
260	1.5	0.3	2.0	4.5	54.2	185.8	160.1	174.4	157.4	153.7	4.1	3.9	2.6
268			2.5	4.2	17.0	43.5	30.8	38.0	35.5	37.3			4.5
273	0.9	−0.2	0.2	0.7‡	0.7‡	−0.8‡	−1.3‡	−5.9‡	1.7‡		5.6	5.1	7.1
281													9.5
286	−0.3	−2.3		0.8	0.2	−0.3	−2.6	−5.7	2.9	−2.5	7.6	7.4	9.3
299	−1.0	−2.4	−0.3	1.3	0.1	−0.4				−3.4	11.5	11.4	3.4
311	1.4	0.5	1.2			−0.6					16.0	15.9	2.7
323	3.7	1.8	1.7			−0.9					10.4	12.3	16.4
334											0.4	1.4	
346												−1.4	
n.m.p.§	−1283	−1290	−1350†	−312	−1645	−4022	−4022	−4022	−4340†	−4460†	−1648	−1700†	

* Normal specific heat (estimated as the mean molecular specific heat of *p*-dinitrobenzene and *p*-xylene) = $12.60 + 0.0991T$ cal. per mole degree.

† Excess sorbate melting. These differences indicate gel capacity to be 0.57 mole of benzene in experiment 19, 3.02 moles of water in experiment 35, 3.11 moles of water in experiment 49, and 0.378 mole of naphthalene in experiment 52.

‡ Heat capacity of sorbate less specific heat of *liquid* water.

§ Normal melting point.

gel are close to those for the 92 per cent saturated gel for an interval, but reach a maximum at a temperature 3°C. lower. Other experiments shown in table 3 indicate that the results are independent of any excess sorbate present. Because of the presence of this frozen excess sorbate, it is unlikely that the remaining sorbate could have supercooled.

CONCLUSION

Substances adsorbed on silica gel melt at temperatures below those at which they would melt in their normal state. Fusion begins at a very low temperature, but the melting temperature rises as increasing amount of melt is formed on the gel. Also, the amount melting increases with the temperature until nearly all the sorbate has melted. In the case of saturated gels this maximum melting occurs with benzene 44°C. below its normal melting point, with water 12°C. below, with naphthalene 40°C. below, and with *p*-nitrotoluene 41°C. below. The amount melting per degree is a reproducible function of the temperature, independent of the rate of cooling or heating, provided the experiments start from the same low temperature. Otherwise there is hysteresis, wherein the amount of solid phase at a given temperature is greater in the experiment starting at the lower temperature.

This is all in accord with the expected behavior of substances condensed in fine capillaries. The negative pressure on the condensed liquid, resulting from surface forces, reduces the escaping tendency of this phase, and a lower temperature is necessary for equilibrium with a solid phase not acted on by surface forces.

SUMMARY

1. The Andrews calibrated heat conduction method was used to measure the heat capacity of substances adsorbed on silica gel. Water, naphthalene, benzene, and *p*-nitrotoluene were investigated in various concentrations.

2. Results from typical experiments for the difference in heat capacity of the adsorbed and normal states of the amount of sorbate associated with 100 g. of activated gel were tabulated. Expressed in this manner, the results were independent of the amount of excess sorbate and over a limited temperature range were independent of concentration for unsaturated gels.

3. Only material in excess of that which saturates the gel melts at its normal melting point. Melting of the adsorbed phase is indicated at lower temperatures by its abnormally large heat capacity. This increment is largest at −12°C. with water, and with the other sorbates at temperatures about 40°C. lower than their normal melting points.

4. These heat capacities were quite reproducible and independent of

the rate of cooling or heating, if started from the same lowest temperature. If previously cooled to a lower temperature, the system had greater heat capacity over certain temperature intervals.

5. The heat of desorption of oxygen was apparent in some experiments. On pure silica gel it was observed up to 240°K. But the larger the amount of sorbate on the gel, the smaller was the capacity of the gel for oxygen.

6. The lowered melting points of the substances adsorbed on silica gel are in agreement with the theory that they are condensed in the capillary voids of the gel and that the forces arising from the highly concave surface of the liquid sorbate are responsible for the lowered escaping tendency of this phase.

REFERENCES

(1) Coolidge: J. Am. Chem. Soc. **46**, 596 (1924).
(2) Jones and Gortner: J. Phys. Chem. **36**, 387 (1932).
(3) Patrick and Land: J. Phys. Chem. **38**, 1201 (1934).
(4) Simon: International Critical Tables.
(5) Smith and Andrews: J. Am. Chem. Soc. **53**, 3644 (1931).
(6) Southard and Andrews: J. Franklin Inst. **207**, 323 (1929).
(7) Southard and Brickwedde: J. Am. Chem. Soc. **55**, 4383 (1933).
(8) Porter and Swain: J. Am. Chem. Soc. **55**, 2792 (1933).

THE EFFECT OF SURFACE FORCES ON MELTING

W. A. KEMPER

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

The preceding paper (5) described calorimetric observations from which the lowered melting temperatures of certain substances adsorbed on silica gel were inferred. In this paper calculations are made of the melting temperatures to be expected if capillary condensation is the cause of adsorption, and the calculations are compared with the calorimetric observations of the preceding paper.

MELTING TEMPERATURES OF ADSORBED SUBSTANCES

It is well known (1) that certain adsorbents are supposed to have capillaries in which vapors condense to liquids, and that the vapor pressure of the condensate increases as the capillaries fill and the stress arising from surface forces decreases. The temperature at which this condensate will freeze depends upon how the solid forms. There are several conceivable ways in which the solid might form, each affecting the stresses on the two phases and consequently the freezing temperature, differently. The solid may form on the walls, narrowing the capillaries. It may form entirely within the body of the liquid, causing but little change in the surface of the liquid. Or, it may form by a process of evaporation and sublimation entirely outside the liquid. In this case the vapor pressure of the liquid remaining would be that of the same amount of liquid with no solid present. The stresses on the solid formed would also be different in these cases. In the last case, the vapor pressure of the small solid particles might be increased by a surface tension of the solid, if such a force exists.

It will here be assumed that: (*1*) *the stress on the unfrozen sorbate is independent of the amount of frozen sorbate present,*[1] and (*2*) *the frozen sorbate is not under any stress from surface forces.* The melting temperature will then be calculated as the temperature at which adsorbed liquid and normal solid have the same vapor pressure.

[1] In this paper the assumptions made are printed in italics.

The vapor pressure of the adsorbed liquid, p, is estimated by the Patrick isotherm (6)

$$X_l v_l = k\left(\frac{p\sigma}{\bar{p}}\right)^n \tag{a}$$

In this, in accord with assumption 1, X_l, the amount of melt on the gel, is used in place of the total amount of sorbate, customarily used in the equation at temperatures above the melting point of the sorbate. v_l, σ, and $\bar{p}$ are the specific volume, the surface tension, and the normal vapor pressure of liquid sorbate at the temperature concerned. The subscript l denotes a property of the liquid state and the overrule ($^-$) refers to the value for the unadsorbed or normal state. k and n are constants which characterize the adsorbent. This equation with the same values of k and n gives the vapor pressure isotherm at any temperature and, with the exception of water, for any sorbate.

The normal vapor pressure of liquid, $\bar{p}$, at temperature T, in terms of its value $\bar{p}_m$ at the normal melting point, is given by the Clapeyron equation

$$\ln \frac{\bar{p}}{\bar{p}_m} = \int_{T_m}^{T} \frac{H_g - H_l}{RT^2}\, dT$$

where H_g and H_l are the heat content of vapor and liquid and R is the gas constant.

With this value of $\bar{p}$, equation a becomes

$$\ln \frac{p}{\bar{p}_m} = \frac{1}{n} \ln \frac{X_l v_l}{k\sigma^n} + \int_{T_m}^{T} \frac{H_g - H_l}{RT^2}\, dT \tag{b}$$

The vapor pressure of solid at the temperature T, in terms of its value at the normal melting point, T_m, also $\bar{p}_m$, is

$$\ln \frac{\bar{p}_s}{\bar{p}_m} = \int_{T_m}^{T} \frac{H_g - H_s}{RT^2}\, dT \tag{c}$$

Equating p and p_s from equations b and c, one obtains the melting temperature, T, corresponding to the amount of melt, X_l:

$$\frac{1}{n} \ln \frac{X_l v_l}{k\sigma^n} = \int_{T_m}^{T} \frac{H_l - H_s}{RT^2}\, dT$$

or

$$\frac{R}{n} \ln \frac{X_l v_l}{k\sigma^n} = \frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^{T} \frac{1}{T^2} \int_{T_m}^{T} (C_{pl} - C_{ps})\, dT^2 \tag{d}$$

where C_{pl} and C_{ps} are the specific heats of liquid and solid sorbate and H_f is the heat of fusion at the normal melting point.

An approximate equation, which neglects the change in the heat of fusion with temperature, is

$$\frac{RT}{n\bar{H}_f} \ln \frac{X_l v_l}{k\sigma^n} = \frac{T - T_m}{T_m} \qquad \text{(d')}$$

With these equations (d or d'), when k and n are known for the adsorbent, one can calculate X_l, the amount of sorbate that can exist as liquid at temperature T. Any sorbate in excess of this is solid. This temperature is termed the melting temperature corresponding to the amount of melted sorbate, X_l.

Calculations of this function, X_l, were made for the four compounds studied in the preceding paper (5). The values of k and n were those which best fitted a set of adsorption isotherms for benzene and water which were obtained in the laboratories of the Silica Gel Corporation on a gel of the same type as ours (7). The similarity of the two gels was verified by comparing their water content when activated, a definite characteristic of a gel. Our activated gel contained 0.0325 g. of water per gram of silica as compared to 0.0324 g. of water per gram of silica reported for the gel from which the adsorption data were obtained.

The following are the resulting values:

$$\log X_l v_l = 1.13 + 0.46 \log \frac{p\sigma}{\bar{p}}$$

for organic sorbates, and

$$\log X_l v_l = -0.145 + 1.05 \log \frac{p\sigma}{\bar{p}}$$

for water where X_l is grams of water (above 3.24 per cent) per 100 grams of activated gel.

The specific heat of *p*-nitrotoluene, which has not been reported, was estimated as the mean of the molar specific heats of *p*-xylene and *p*-dinitrobenzene. The values obtained were $C_{ps} = 12.6 + 0.0991T$ and $C_{pl} = 21.17 + 0.085T$ cal. per °C. mole.

The other data for the calculations were obtained from accredited sources.

The actual values of X_l were not calculated from the observations in the previous report. However, the values of X_l, calculated from equation d, are shown in figure 1. Since the amount melting increases with temperature until melting is complete, the observed temperature of maximum melting can be compared with calculations of the temperature at which the sorbate would be completely melted. The temperature at which the

heat capacity was a maximum was taken as the temperature of maximum melting. Values of X_l equal to the total amount of sorbate present in these experiments are indicated on the curves by the horizontal lines. A comparison of these two is given in table 1.

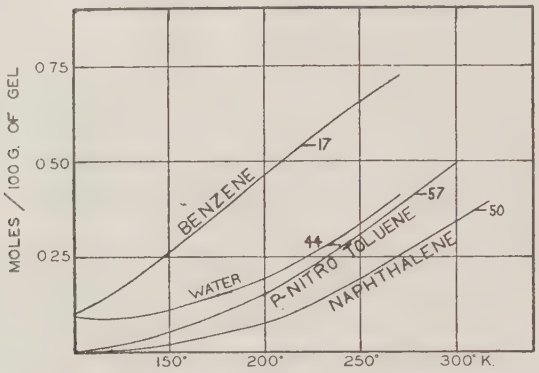

FIG. 1. Calculated amount of unfrozen sorbate. Numbered horizontal line indicates total sorbate present in the corresponding experiment

TABLE 1

Comparison of observed temperature of maximum melting with calculated temperature at which the sorbate would be completely melted

SUBSTANCE	EXPERIMENT NO.	CALCULATED TEMPERATURE AT WHICH MELTING IS COMPLETE	OBSERVED TEMPERATURE OF MAXIMUM HEAT CAPACITY
		°K.	°K.
Benzene	17	219	229
Water	44	231	260
Naphthalene	50	307	313
p-Nitrotoluene	57	278	283

The observed temperatures are not as low as the calculated values. The discrepancy is believed to be due to a hysteresis. The difference is largest in the case of water, and water is known to show more hysteresis than other sorbates.

CALCULATIONS OF THE APPARENT HEAT CAPACITY OF THE ADSORBED PHASE

In the previous paper (5) values were obtained for the difference in apparent heat capacity of the adsorbed phase and normal solid sorbate. If the theory of capillarity is correct, this difference consists of the following terms:

(1) $(C_{pl} - C_{ps})X_l$, the difference in heat capacity of adsorbed liquid and normal solid times the amount of adsorbed liquid.

(2) $(H_l - H_s)\dfrac{dX_l}{dT}$, the heat of fusion times the amount of melting per degree increase in temperature.

(3) $X_l\left(\dfrac{\partial H_l}{\partial P}\right)\dfrac{dP_l}{dT}$, the heat of compression for the change in pressure accompanying one degree rise in temperature.

(4) $-H_\omega\dfrac{d\omega}{dT}$, minus the heat of wetting per unit area times the amount of surface newly wetted by melt per degree rise in temperature.

(5) $\omega\dfrac{dH_\omega}{dT}$, the heat capacity of the surface layer.

The evaluation of each of these terms for the amount of sorbate contained on 100 g. of silica gel follows. In the calculations the *change in density of adsorbed liquid with pressure will be neglected.*

The heat capacity of a liquid is independent of pressure, if *thermal expansion is assumed to be linear.* For

$$\frac{\partial C_{pl}}{\partial P} = T\frac{\partial^2 v_l}{\partial T^2} = 0$$

Hence the first term is

$$(\bar{C}_{pl} - \bar{C}_{ps})X_l \tag{1}$$

The amount melting per degree is obtained from the derivative of equation d with respect to temperature, σ being represented by $A + BT$ and $\dfrac{1}{v_l}\dfrac{\partial v_l}{\partial T}$ by E, the coefficient of cubical expansion. The expression is

$$\frac{dX_l}{dT} = \frac{nX_l}{RT^2}\left[\bar{H}_f + \int_{T_m}^{T}(C_{pl} - C_{ps})\,dT + \frac{BRT^2}{A + BT}\right] - EX_l \tag{e}$$

The heat of fusion is

$$H_l - H_s = \bar{H}_f + \int_{T_m}^{T}(C_{pl} - C_{ps})\,dT + \int_0^{P_l}\left(\frac{\partial H_l}{\partial P}\right)_T dP_l$$

where P_l is the hydrostatic pressure on the adsorbed liquid.

The value of the last term, the heat of expansion, is obtained from the equation of state:

$$\left(\frac{\partial H_l}{\partial P}\right)_T = v_l - T\left(\frac{\partial v_l}{\partial T}\right)_P$$

The second term of this is neglected so that

$$\int_0^{P_l}\left(\frac{\partial H_l}{\partial P}\right)_T dP_l = v_l P_l$$

In order to change from the auxiliary function P_l to T the following procedure can be used: P_l is related to the vapor pressure of the liquid by the equation for the vapor pressure of a liquid under hydrostatic pressure,

$$RT \ln p/\bar{p} = v_l P_l$$

Then, using the value of $p/\bar{p}$ from equation a, one obtains

$$v_l P_l = \frac{RT}{n} \ln \frac{X_l v_l}{k\sigma^n}$$

Finally by means of equation d the value of $v_l P_l$ is found in terms of T.

$$v_l P_l = \frac{\bar{H}_f T}{T_m} - \bar{H}_f + T \int_{T_m}^{T} \frac{1}{T^2} \int_{T_m}^{T} (C_{pl} - C_{ps})\, dT^2 \qquad (f)$$

This is a fundamental equation and also could have been obtained from

$$v_l dP_l = \frac{H_l - H_s}{T} dT$$

which results from equating

$$dF_l = dF_s$$

where F denotes free energy.

Using equation f, and simplifying, one then obtains for the heat of fusion,

$$H_l - H_s = \frac{\bar{H}_f T}{T_m} + T \int_{T_m}^{T} \frac{C_{pl} - C_{ps}}{T} dT \qquad (g)$$

The second term of the heat capacity, $(H_l - H_s) \dfrac{dX_l}{d\bar{T}}$, can now be obtained by multiplying equations e and g.

As the amount of liquid is increased by melting, the negative pressure decreases and the liquid is subject to compression. The increase of pressure on the liquid with temperature is found by taking the derivative of equation f with respect to temperature. When v_l is represented by $v_l = v_{l_0}(1 + E\Delta T)$, the equation of state becomes

$$\left(\frac{\partial H_l}{\partial P}\right)_T = \frac{1 + ET_0}{1 + E\Delta T} v_l$$

(This coefficient of v_l is small and was neglected above in calculating the correction to the heat of fusion for the expansion of newly melted liquid.) The heat of compression is then

$$X_l \frac{dP_l}{dT}\left(\frac{\partial H_l}{\partial P}\right)_T = X_l \frac{1 - ET_0}{1 + E\Delta T}\left[\left(\frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^{T} \frac{1}{T^2} \int_{T_m}^{T} (C_{pl} - C_{ps})\, dT^2\right)\left(\frac{1 - ET_0}{1 + E\Delta T}\right) + \frac{\bar{H}_f}{T} + \frac{1}{T} \int_{T_m}^{T} (C_{pl} - C_{ps})\, dT\right] \qquad (3)$$

The heat content per unit area of surface,

$$H_\omega = \sigma - T\frac{d\sigma}{dT} = A$$

where A was defined by $\sigma = A + BT$.

Activated silica gel is assumed to be covered with a monomolecular film of water. As melted sorbate fills the capillaries, this water–air interface is replaced by a water–sorbate interface. The heat evolved will be the heat content of the water–air interface less that of the water–sorbate interface. By Antonow's rule (2), which is valid if the molecules of the second liquid are not oriented at the water interface, this difference is equal to the heat content of the sorbate–air interface, which is A times the area.

The change in area of surface, ω, is calculated by considering a differential element of the capillary as a cylinder. The element of volume is $\pi r^2 dh$ and the element of area is $2\pi r dh$. Hence

$$\frac{d\omega}{v_l\, dX_l} = \frac{2}{r}$$

and since

$$P_l = -\frac{2\sigma}{r}$$

$$\frac{d\omega}{dT} = -\frac{v_l P_l}{\sigma}\frac{dX_l}{dT}$$

Using the value of $v_l p_l$ from equation f, one obtains for the fourth term,

$$H_\omega \frac{d\omega}{dT} = \frac{AT}{A + BT}\left[\frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^{T}(C_{pl} - C_{ps})\, dT^2\right]\frac{dX_l}{dT} \qquad (4)$$

Since the heat content of the surface,

$$H_\omega = \sigma - T\frac{d\sigma}{dT} = A$$

and A is independent of the temperature,

$$\omega\frac{dH_\omega}{dT} = 0 \qquad (5)$$

The sum of the above five terms represents, on the basis of the assumptions that have been made, the apparent heat capacity of the adsorbed substance in excess of its heat capacity in its normal solid state, if capillarity is the cause of its adsorption.

Calculation of all of these quantities for the four substances reported in

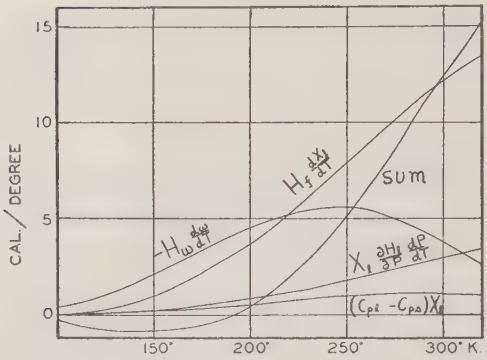

FIG. 2. Calculated component parts of extra heat capacity of naphthalene associated with 100 g. of activated gel

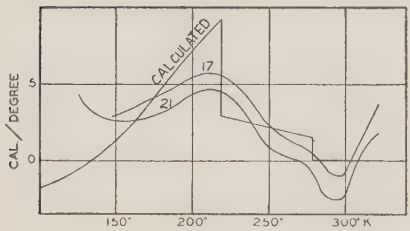

FIG. 3

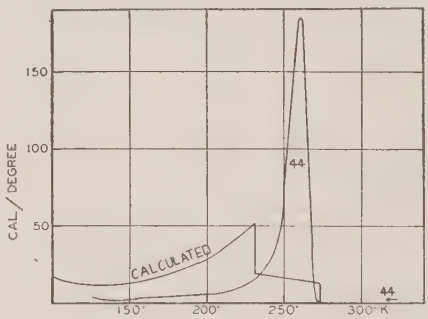

FIG. 4

FIG. 3. Additional heat capacity of benzene adsorbed on 100 g. of gel
FIG. 4. Additional heat capacity of water adsorbed on 100 g. of gel

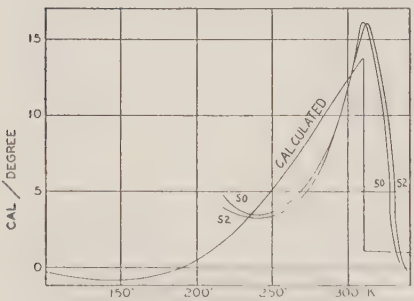

FIG. 5

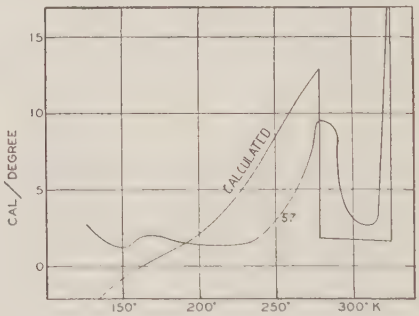

FIG. 6

FIG. 5. Additional heat capacity of naphthalene adsorbed on 100 g. of gel
FIG. 6. Additional heat capacity of *p*-nitrotoluene adsorbed on 100 g. of gel

the previous paper has been made. Figure 2 shows the calculated increase in heat capacity of adsorbed naphthalene and the components from which it was evaluated. Figures 3 to 6 show the calculated and observed values for the increase in heat capacity of benzene, water, naphthalene, and *p*-nitrotoluene when adsorbed on the gel.

The observed values lie on the high temperature side of the calculated values, and once more the poorest agreement found is in the case of water. The hysteresis would cause the values observed on heating to lag behind those calculated for equilibrium conditions.

DISCUSSION

One might suppose that the small size of the solid particles would have some effect on the melting point. Meissner (4) observed a melting-point lowering of a fraction of a degree with crystals 0.8 μ thick. However, Meissner's experiments and most of the theoretical treatments have been concerned with a situation in which the particles were within the melt. In the present experiments the simplifying assumption has been made that the solid has normal vapor pressure. Kubelka (3), who discussed various theoretical equations, proposed a similar simplification for sorbates in silica gel or charcoal. He derived an approximate equation for the melting-point lowering as a function of the radius of the capillaries, in which he assumes that the heat of fusion is constant with the temperature.

In this paper we have calculated the temperature at which normal solid is in equilibrium with an adsorbed phase, which follows the Patrick isotherm modified for a supercooled liquid. It is, of course, possible that the use of some other isotherm equation based upon some other theory of adsorption might give equally good results. However, the assumptions made contain intrinsically a good deal of the idea of capillarity. To this extent, accordingly, such agreement as exists between the calculations of the present paper and the calorimetric observations lends some support to the theory of capillary condensation. A closer agreement could not be expected without eliminating the hysteresis phenomenon.

SUMMARY

1. The Patrick equation for adsorption was extended below the normal melting point of the sorbate by using as values for normal vapor pressure, surface tension, and specific volume, those of supercooled liquid sorbate.

2. A general equation was obtained for the melting temperature of substances condensed in porous adsorbents.

3. Calculations were made of the melting temperatures of the four substances adsorbed on silica gel reported in the previous paper (5). The calculations used only two constants characterizing the gel, k and n of the Patrick equation. The values employed for these were obtained from

a study of adsorption isotherms of benzene and water on this gel at higher temperatures. The temperatures at which the last portions of the sorbates were calculated to have melted averaged only 14°C. lower than the temperatures at which the maxima in the heat capacities of the systems had been observed. It is believed that the calculated temperatures are lower because of hysteresis.

4. Further equations were derived from the various terms which compose the difference between heat capacity of the sorbate in the adsorbed state and in its normal solid state.

5. The results of these calculations were compared with the observations reported in the previous paper (5).

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REFERENCES

(1) Friedel, G.: Bull. soc. franç. minéral. **21,** 5 (1898).
(2) Freundlich: Colloid and Capillary Chemistry, 3rd edition, translated by Hatfield, p. 99. E. P. Dutton and Co., New York.
(3) Kubelka: Z. Elektrochem. **38,** 611 (1932).
(4) Meissner: Z. anorg. allgem. Chem. **110,** 169 (1920).
(5) Patrick and Kemper: J. Phys. Chem. **41,** 369 (1938).
(6) Patrick and McGavack: J. Am. Chem. Soc. **42,** 946 (1920).
(7) Silica Gel Corporation: Unpublished reports Nos. 1001A, 1004, 1009, 1010 (1925, 1926).

VITA

William Alexander Kemper was born on January 1, 1911, in Baltimore, Maryland. There he attended the public schools and graduated from the Forest Park High School in 1927. The following fall, he entered The Johns Hopkins University and began graduate work in chemistry in 1929 under the new plan. In his first year he received a University Scholarship, in 1929–1930, a Charles Carroll Fulton Scholarship, and a Trustees' Grant in 1933–1934. He has been in the research department of the Consolidated Gas and Electric Light and Power Company of Baltimore since 1931.